attributed to the tendency of nickel(II) to attain six-coordination, with more favorable bond energy resulting from the formation of four Ni–O bonds than from two $Ni\text{–}NO_2$ bonds. In contrast with this the anions in $Ni\{(n\text{-}C_4H_9)_3P\}_2(NO_2)_2$ are bonded through nitrogen.[21] However, nickel complexes with trialkylphosphines are usually diamagnetic *trans*-planar,[22] and the spin pairing would tend to favor $M\text{–}NO_2$ bonding, since nitro groups lie well toward the stronger end of the spectrochemical series, as compared with nitrito groups.

It is apparent from this and other recent work that the nitrite ion is a very versatile ligand and that further studies are necessary to elucidate the factors influencing its method of coordination.

Acknowledgment.—We thank the D.S.I.R. for a Research Studentship to M. A. H.

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[22] K. A. Jensen, *Z. anorg. allgem. Chem.*, **229**, 265 (1936).

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Ligand Field Strength of the Nitrogen End of Cyanide and Structures of Cubic Cyanide Polymers[1]

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Near-infrared, visible, and ultraviolet spectra were determined for potassium nickel ferrocyanide, potassium nickel cobalticyanide, and some related compounds. These materials involve Ni^{2+} octahedrally coordinated to the nitrogen end of cyanide, and straightforward analysis of the spectral data yields the ligand field strength for this ligand. The Dq value ranges between 1010 and 950 cm.$^{-1}$ and places the nitrogen end of cyanide below NH_3 on the spectrochemical series. The value of Dq noted above was used in an attempt to explain the structures of mixed cyanide polymers (*e.g.*, $KMnFe(CN)_6$) by calculation of site preference energies which were primarily based on crystal field stabilization energies. The site preference energies show a good correlation with actual structures. Linkage isomerism was predicted and found for $KFeCr(CN)_6$, which is less stable than $KCrFe(CN)_6$. The former compound apparently involves $Fe^{II}\text{—}N\equiv C\text{—}Cr^{III}$ linkages while the latter involves $Cr^{III}\text{—}N\equiv C\text{—}Fe^{II}$.

Introduction

Among the oldest known synthetic inorganic complexes are the cyanide polymers such as the Prussian blues. Keggin, Miles, and others have shown that these compounds occur with face-centered cubic lattices.[3] The structures involve transition metals in carbon and nitrogen octahedra. For example, recent studies on Prussian blue leave little doubt that Fe^{3+} is nitrogen-coordinated, while Fe^{2+} is carbon-coordinated.[4] Clearly, these polymeric cyanides afford a unique opportunity to study the behavior of the nitrogen end of cyanide as a ligand. It has not been possible to observe metal–$N\equiv C$ coordination in monomeric transition metal cyanide complexes because of the great affinity of these metals for the carbon end. Our objective was to determine the ligand field strength of the nitrogen end of cyanide, which is relevant to an understanding of structures of simple and polymeric cyanide complexes. Also, we were interested in comparing the spectra of polymeric cyanides with those of bridge addition compounds (*e.g.*, $K_4Fe(CNBF_3)_6$).[5]

Experimental

Analyses.—Before analysis samples were dried by gentle heating *in vacuo* and were subsequently handled in a water-free nitrogen atmosphere. Alkali metal was determined by Samuelson's ion-exchange procedure,[6] nickel gravimetrically as the dimethylglyoximate, and iron and chromium by modifications of published titrimetric procedures.[7] C, H, and N analyses were performed by Schwarzkopf Microanalytical Laboratory.

Spectroscopic Procedures.—Near-infrared, visible, and ultraviolet spectra were obtained with a Cary Model 14 recording spectrophotometer. The mull transmittance technique was employed for Fluorolube or water suspensions of all samples.[8] In addition, most of the spectra were also determined by diffuse reflectance with the Cary integrating sphere attachment. Infrared spectra in the $C\equiv N$ stretch region were obtained on a prism-grating Beckman IR 9. The samples were in oil or water mulls.

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[2] N.S.F. Undergraduate Summer Research Participant, 1964.

[3] (a) J. F. Keggin and F. D. Miles, *Nature*, **137**, 577 (1936); (b) R. Rigamonti, *Gazz. chim. ital.*, **67**, 137 (1937); (c) R. Rigamonti, *ibid.*, **67**, 146 (1937); (d) A. K. van Bever, *Rec. trav. chim.*, **57**, 1259 (1938); (e) R. Rigamonti, *Gazz. chim. ital.*, **68**, 803 (1938); (f) M. A. Rollier and E. Arreghini, *ibid.*, **69**, 499 (1939); (g) M. A. Rollier and G. Cesoni, *ibid.*, **69**, 674 (1939); (h) H. B. Weiser, W. O. Milligan, and J. B. Bates, *J. Phys. Chem.*, **46**, 99 (1942); (i) A. Ferrari, M. E. Tani, and G. Magnano, *Gazz. chim. ital.*, **89**, 2512 (1959).

[4] (a) G. Emschwiller, *Compt. rend.*, **238**, 1414 (1954); (b) M. B. Robin, *Inorg. Chem.*, **1**, 337 (1962); (c) J. F. Duncan and P. W. R. Wigley, *J. Chem. Soc.*, 1120 (1963).

[5] (a) D. F. Shriver, *J. Am. Chem. Soc.*, **85**, 1405 (1963); (b) *ibid.*, **84**, 4610 (1962).

[6] O. Samuelson, "Ion Exchangers in Analytical Chemistry," John Wiley and Sons, New York, N. Y., 1953, p. 156.

[7] (a) I. M. Kolthoff and H. Menzel, "Volumetric Analysis," Vol. 2, John Wiley and Sons, New York, N. Y., 1929, p. 485; (b) W. F. Hillebrand, G. E. F. Lundell, H. A. Bright, and J. I. Hoffman, "Applied Inorganic Analysis," 2nd Ed., John Wiley and Sons, New York, N. Y., p. 527.

[8] F. A. Cotton, D. M. L. Goodgame, M. Goodgame, and A. Sacco, *J. Am. Chem. Soc.*, **83**, 4157 (1961).

Simple Cyanide Complexes.—Monomeric cyanide complexes used in this work were synthesized and purified according to directions given in the following references: $K_3Co(CN)_6$,[9] $K_3Cr(CN)_6$,[10] $K_3Mn(CN)_6$,[11] and $K_4Ru(CN)_6 \cdot 3H_2O$.[12]

$K_2NiFe(CN)_6$.—$K_4Fe(CN)_6 \cdot 3H_2O$ (21 g., 0.50 mole) dissolved in 100 ml. of H_2O was added to a solution of 14.55 g. (0.50 mole) of $Ni(NO_3)_2 \cdot 6H_2O$ and 2 g. of KCl in 85 ml. of H_2O. Freshly-boiled distilled water was used for these solutions and the preparation was carried out in a nitrogen-filled glove bag. The mixture was filtered in a Büchner funnel which was covered with a tightly-fitting rubber stopper through which nitrogen was circulated. The precipitate was washed first with 20 ml. of KCl solution (0.2 g. of KCl in 20 ml. of H_2O), and final washing was done with five 40-ml. portions of freshly-boiled water. Wash water was introduced by means of a hypodermic syringe through a serum bottle cap fitted to the rubber stopper. During the filtration the precipitate changed color from medium to light aqua. It was dried in the dark under vacuum at room temperature for 72 hr. The dark green solid which resulted was finely ground and dried under vacuum for 24 hr. at 60°. All transfer operations were carried out in a nitrogen-filled glove bag and exposure to light was minimized. *Anal.* Calcd. for $K_2NiFe(CN)_6$: C, 20.65; H, 0.0; N, 24.09; K, 22.4; Ni, 16.82; Fe, 15.88. Found: C, 20.37; H, 0.0; N, 23.87; K, 22.7; Ni, 15.69; Fe, 14.67. An X-ray powder pattern of this sample (I) indicated it was poorly crystalline, but vibrational and electronic spectra were nearly identical with those of other preparations which gave well-defined powder patterns.

Another sample (II) was prepared in a similar manner, but without exclusion of air and dialysis for 80 hr. was substituted for the filtration and washing. *Anal.* Found: C, 19.85; H, 0.90; N, 24.09; Ni, 18.97. The X-ray powder pattern of this sample was indexed on the basis of a face-centered cubic lattice with a = 9.96 Å., which agrees with the literature.[3c]

$KNiCo(CN)_6$.—Equimolar portions of aqueous $K_3Co(CN)_6$ and nickel nitrate solution were mixed and the precipitate was collected and washed in a Büchner funnel. Care was taken to exclude bright light during these operations. Final drying of the sample (III) was performed at 40° *in vacuo*. *Anal.* Calcd. for $KNiCo(CN)_6$: C, 23.03; H, 0.0; N, 26.86; K, 12.5; Ni, 18.76. Found: C, 16.60; H, 1.07; N, 22.50: K, 21.1; Ni, 15.69. The analyses and appearance of an infrared band of medium intensity around 2140 cm.$^{-1}$ led us to suspect the presence of excess $Co(CN)_6^{-3}$ *i.e.*, nonbridging cyanide) in this sample. Therefore, we prepared samples with an excess of nickel, but the 2140 cm.$^{-1}$ band was not diminished. It is possible that this absorption does not represent a fundamental vibrational transition. One of these samples (IV) was prepared with Ni^{2+} and $Co(CN)_6^{3-}$ in a 4:3 mole ratio and excess salt was removed by dialysis. *Anal.* Found: C, 19.00; H, 0.75; N, 22.19; K, *ca.* 1.1; Ni, 20.70. Potassium nickel cobalticyanide is blue-green (aqua) when dried. A powder pattern of the dialyzed material showed that it is isomorphous with $K_2NiFe(CN)_6$.

Nickel chromicyanide was prepared by adding a solution of 2.91 g. (0.1 mole) of $NiNO_3 \cdot 6H_2O$ in 30 ml. of water to 3.25 g. (0.01 mole) of $K_3Cr(CN)_6$ in 25 ml. of water. The blue-green precipitate was dialyzed for 60 hr. Potassium analysis of the dried product showed that only *ca.* 1% K was present. The material became dark greenish black when dried. An X-ray powder pattern showed that it was isomorphous with the other cyanide polymers.

Other $Co(CN)_6^{3-}$ and $Cr(CN)_6^{3-}$ Polymers.—A series of first-row transition metal salts of $Co(CN)_6^{3-}$ was prepared by mixing solutions of the various cations with $K_3Co(CN)_6$ solution in a 1:1 mole ratio. The products were filtered and washed with water, and infrared spectra of the wet suspensions were taken within 1.5 hr. of preparation. These samples were then dried at 70° for 24 hr., after which infrared spectra of Nujol and water mulls were again determined. The chromicyanides were investigated by similar procedures except that a 3:2 molar ratio of chromicyanide to metal was employed and samples were dried at 100°. It is reported in the literature that compounds prepared by the foregoing procedures contain small amounts of potassium but approach compositions such as $Mn_3[Cr(CN)_6]_2$.[13] In agreement with this we found only 0.72% potassium in one sample of nickel chromicyanide.

In an attempt to prepare a sample near a composition of $KFeCr(CN)_6$ we washed a sample of ferrous chromicyanide only briefly because qualitative tests had shown that $K_3Cr(CN)_6$ could be leached from freshly precipitated samples. This material contained 7.7% K, 18.60% C, and 21.17% N. Infrared spectra showed the presence of water in this material. The analytical data indicate a ratio of potassium to chromicyanide of 0.77:1.

Efforts to prepare well-defined cyanide polymers from $K_3Mn(CN)_6$ were unsuccessful. When ferrous ion was added to $Mn(CN)_6^{3-}$ a deep blue precipitate formed which displayed a visible absorption maximum at 735 mμ and a strong C≡N stretch frequency at 2086 cm.$^{-1}$. These spectral data indicate that Prussian blue was probably formed since the reported absorptions are 780 mμ[4b] and 2085 cm.$^{-1}$.[4a] Fe^{3+}, Co^{2+}, and Zn^{2+} gave brown precipitates with $Mn(CN)_6^{3-}$. These precipitates displayed broad infrared absorption in the C≡N stretch region, which indicates ill-defined products. The precipitate formed with Zn^{2+} gave a strong odor of HCN.

Results and Discussion

X-Ray powder diffraction studies on $K_2NiFe(CN)_6$ indicate a face-centered cubic lattice with a = 9.96 Å. (see Figure 1).[3c] The probable space group is Fm3m with four Fe^{2+} at positions of m3m symmetry (0, 0, 0; etc.) and four Ni^{2+} in a second set of m3m symmetry ($^1/_2$, $^1/_2$, $^1/_2$; etc.). The $C{\equiv}N^-$ groups occur along lines connecting Ni^{2+} to nearest Fe^{2+} neighbors, but due to similarities in atomic scattering factors, it was

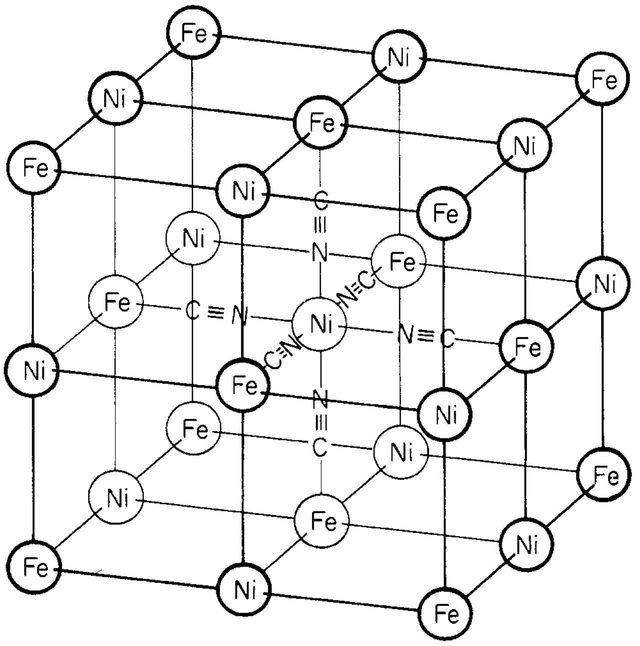

Figure 1.—The structure of $K_2NiFe(CN)_6$. Potassium ions and most of the C≡N groups are not shown. Their positions are described in the text.

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[9] J. H. Bigelow, *Inorg. Syn.*, **2**, 225 (1946).

[10] J. H. Bigelow, *ibid.*, **2**, 203 (1946).

[11] J. A. Lower and W. C. Fernelius, *ibid.*, **2**, 213 (1946).

[12] Gmelin, "Handbuch der Anorganischen Chemie," No. 63, Verlag Chemie, Berlin, 1938, p. 101.

[13] F. Cruser and E. H. Miller, *J. Am. Chem. Soc.*, **28**, 1132 (1906).

not possible to decide whether iron occurs in carbon octahedra and nickel in nitrogen octahedra or *vice versa*. In addition, eight potassium ions occupy sites of $\bar{4}3m$ symmetry ($^1/_4$, $^1/_4$, $^1/_4$; $^3/_4$, $^3/_4$, $^3/_4$; etc.). The variable composition of these salts arises because transition metals may substitute for potassium ions; for example, two K^+ ions may be replaced by a Ni^{2+} ion. Since no reduction in crystal symmetry is noted upon such substitution, the multiply-charged transition metal ions must occupy $\bar{4}3m$ positions in a random or nearly random fashion.

Evidence for the Fe—C≡N—Ni arrangement was obtained by Emschwiller, who investigated a series of heavy metal ferrocyanides and found that the C≡N stretching frequency of nickel ferrocyanide falls in the same range as other members of this series.[4a] The infrared spectrum of $K_2NiFe(CN)_6$ contains a single fairly narrow band at 2100 cm.$^{-1}$. This result is consistent with the octahedral site symmetry of the $Fe(CN)_6^{4-}$ groups, for which a single infrared active C≡N stretch vibration of T_{1u} symmetry is expected. In addition, this absorption frequency is quite similar to that of copper ferrocyanide (2108 cm.$^{-1}$—our determination), which is known from magnetic data to involve Fe–C bonding.[14]

Perhaps the best evidence for Ni–N bonding in $K_2NiFe(CN)_6$ is its near-infrared and visible spectrum, which is typical of octahedrally-coordinated Ni^{2+} (Figure 2). The near-infrared absorption indicates a *Dq* value of *ca.* 1000 cm.$^{-1}$, which is far too low for the carbon end of cyanide but quite reasonable for the nitrogen end. The spectra were obtained for materials ranging from aqueous suspensions to anhydrous mulls, but no consistent differences were observed. This finding agrees with the structure depicted in Figure 1 and helps to substantiate the proposal that there is no significant amount of Ni^{2+} in $\bar{4}3m$ sites (presumably Ni^{2+} in these sites would be aquated in the hydrous material).

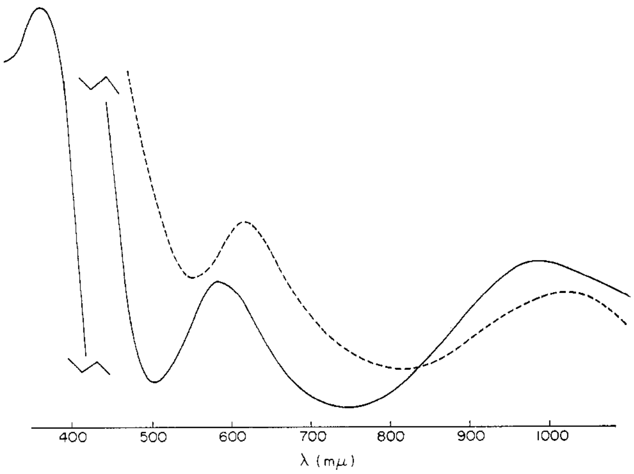

Figure 2.—Near-infrared visible and ultraviolet spectra of $KNiCo(CN)_6$ (———) and $K_2NiFe(CN)_6$ (- - - -).

Interpretation of Electronic Spectra.—Spectra of octahedral Ni(II) complexes display three spin-allowed d–d transitions.[15] The low-frequency $^3A_{2g} \rightarrow {}^3T_{2g}$ band at *ca.* 1000 mμ and the visible $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transition at *ca.* 600 mμ were clearly evident and have been mentioned above. By use of an average ^3F–^3P separation of 15,614 cm.$^{-1}$ for Ni(II)(g)[16] the position of the third band, $^3A_{2g} \rightarrow {}^3T_{2u}(P)$, is estimated to be *ca.* 372 mμ. The band at 310 mμ for $K_2NiFe(CN)_6$ is in rather poor agreement with this estimate, but comparison with zinc ferrocyanide, which has an absorption at 310 mμ, and also comparison with spectra of aqueous ferrocyanide,[17] leaves little doubt that this absorption represents the $^1A_{1g} \rightarrow {}^1T_{1g}$ d–d transition for $Fe(CN)_6^{-4}$, which masks the $^3A_{2g} \rightarrow {}^3T_{2u}(P)$ nickel band. A band does occur at *ca.* 370 mμ in potassium nickel chromicyanide, $KNiCo(CN)_6$, and potassium nickel hexacyanoruthenate(II), but as described below this band is probably not the $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transition.

It is clearly evident from Table I that the precision with which the band positions are located is not high. The following factors are probably the major sources of error: (1) particle size effects which led to variable scattering and internal absorption both for mull transmittance and reflectance[18]; (2) low intensity and breadth of the near-infrared and visible bands which generally necessitated the use of a 0 to 0.2 absorbance slide wire and wide slit settings; (3) variable composition of the samples. One of the major problems with some ferrocyanide samples appeared to be slight oxidation. Despite these difficulties, average values may be assigned for the transitions, and it does appear that *Dq* for the nitrogen in ferrocyanide (*ca.* 950 cm.$^{-1}$) is lower than in the other complexes (*ca.* 1010 cm.$^{-1}$). For the potassium nickel cobalticyanide samples average values of the transitions are $^3A_{2g} \rightarrow {}^3T_{2g}$, 10,100 cm.$^{-1}$; $^3A_{2g} \rightarrow {}^3T_{2u}(F)$, 16,700 cm.$^{-1}$; and possibly $^3A_{2g} \rightarrow {}^3T_{2u}(P)$, 27,200 cm.$^{-1}$. Calculated values for the last two transitions using the ^3F–^3P separation for Ni^{2+} (g) are 19,030 and 26,890 cm.$^{-1}$.

The discrepancy between observed and calculated bands is greater than what is usually observed for Ni^{2+} complexes.[19] In addition, the intensity of the 370 mμ (27,000 cm.$^{-1}$) band is unusually high for a nickel d–d transition, and the F–P term separation calculated from this band does not represent a significant reduction below the gas phase value. In view of the uncertain origin of this band only the two lower energy bands were used to find the percentage reduction in the F–P term separation (β). A value of 50% for β leads to a calculated energy of 16,700 cm.$^{-1}$ (597 mμ) for the $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ band of potassium nickel chromicyanide and the corresponding cobalticyanide and

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[14] (a) J. Richardson and N. Elliott, *J. Am. Chem. Soc.*, **62**, 3182 (1940); (b) P. G. Salvadeo, *Gazz. chim. ital.*, **89**, 2184 (1959).

[15] C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 261.

[16] C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Addison-Wesley, Inc., Reading, Mass., 1962, p. 41.

[17] (a) Reference 16, p. 293; (b) H. B. Gray and N. A. Beach, *J. Am. Chem. Soc.*, **85**, 2922 (1963).

[18] N. T. Melamed, *J. Appl. Phys.*, **34**, 560 (1963).

[19] O. Bostrup and C. K. Jørgensen, *Acta Chem. Scand.*, **11**, 1223 (1957).

TABLE I

ELECTRONIC SPECTRA

	Compound	Electronic spectrum, mμ Reflectance	Transmittance
I	$K_2NiFe(CN)_6$	1080	
		615	
	$K_2NiFe(CN)_6$[a]	1100	1045
		620	600
			(310)
II	$K_2NiFe(CN)_6$		960–1025
			590–620
III	$KNiCo(CN)_6$		990
			595
			368
IV	Potassium nickel		998
	cobalticyanide		603
			366
V	Potassium nickel		990
	chromicyanide		595
			370
VI	Potassium nickel		990
	ruthenocyanide		610
			365

[a] This sample was prepared in a manner similar to I.

TABLE II

CYANIDE STRETCHING FREQUENCIES

Compoound	Infrared absorption, cm.$^{-1}$
Ferrocyanides	
Cr^{3+}[a]	2092 s
Cu^{2+}	2108 s
Chromicyanides	
Mn^{2+}	2159 s
Fe^{2+}	2168 s, 2114 w
Co^{2+}	2194 mw, 2173 s, 2138 w
Ni^{2+}	2172 s
Cu^{2+}	2182 m, 2120 s
Zn^{2+}	2178 s
Cobalticyanides	
Mn^{2+}	2168 s
Fe^{2+}	2190 sh, 2175 s, 2145 sh
Co^{2+}	2173 s, 2138 w, 2094 mw
Ni^{2+}	2187 s, 2141 mw
Cu^{2+}	2191 s
Zn^{2+}	2182 s, 2145 w

[a] The formulation as a ferrocyanide was inferred from the infrared spectrum. The sample was originally potassium ferrous chromicyanide. s, strong; m, medium; w, weak; sh, shoulder.

ruthenocyanide, for which the observed band is at *ca.* 600 mμ. This same value for β leads to a calculated energy of 16,053 cm.$^{-1}$ (621 mμ) for $K_2NiFe(CN)_6$; the observed value is 620 mμ.

In keeping with previous speculation,[5] the nitrogen end of cyanide has a ligand field strength lower than ammonia and about the same as nitrogen in similar bonding environments, NCS^- and NCO^-.[20]

Inductive Effects.—Previously, one of us found that addition of BF_3 to cyanide complexes leads to small changes in d–d transitions. In particular, a mull transmittance spectrum of $K_4Fe(CN)_6 \cdot 3H_2O$ displayed a band at 30,700 cm.$^{-1}$, and this apparently corresponds to the $^1A_{1g} \rightarrow {}^1T_{1g}$ d–d transition of aqueous $Fe(CN)_6^{4-}$.[17] Upon formation of a complex with the gross composition $K_4Fe(CN)_6 \cdot 5.3BF_3$, this band moved to 31,700 cm.$^{-1}$. An apparent increase in ligand field strength also occurred when the nitrogen end of cyanide was coordinated to another metal, *e.g.*, zinc ferrocyanide has an absorption at 32,300 cm.$^{-1}$.

Interpretation of Infrared Spectra.—Structural information on metal cyanide polymers containing two different transition metals has been obtained from magnetic data for a number of favorable cases.[14] Also, structural inferences have been made by Emschwiller on the basis of infrared data.[4a] In order to extend the available structural information we investigated the infrared spectra of some cobalticyanides and chromicyanides. The observed frequencies are collected in Table II.

It is well known that the cyanide stretching frequency is affected by the oxidation state of the central metal.[21] For example, central metals with +3 oxidation states give rise to a C≡N stretch near 2130 cm.$^{-1}$ (*e.g.*, $K_3Cr(CN)_6$, 2135; $K_3Mn(CN)_6$, 2125; $K_3Fe(CN)_6$, 2125; $K_3Co(CN)_6$, 2143, 2129, 2126 cm.$^{-1}$), whereas +2 central metals lead to a lower value around 2050 cm.$^{-1}$ (*e.g.*, $K_4Mn(CN)_6$, 2060; $K_4Fe(CN)_6$, *ca.* 2047 cm.$^{-1}$).[21] In addition, the formation of cyanide bridges leads to a modest (*ca.* 30 cm.$^{-1}$) increase in C≡N stretching frequencies. Thus, we expect to be able to distinguish a +3 metal from a +2 metal in the carbon holes of a cyanide polymer, and the results in Table II are consistent with this view. However, these data leave unanswered the question of which metal is involved in carbon coordination. The C≡N stretching frequencies of chromicyanides and cobalticyanides roughly fall in the order $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$, and with one exception Emschwiller's more limited data on the ferrocyanides fall in the same order. It is interesting that this order parallels the "natural order of stability" for bivalent transition metal complexes (*e.g.*, ref. 29, p. 16). The existence of spurious bands of appreciable intensity in cobalt chromicyanide, copper chromicyanide, and cobalt cobalticyanide leads us to believe that some cyanide flipping has occurred in these samples.

Structures of Simple Cyanide Complexes.—It is generally accepted that simple cyanide complexes such as $Fe(CN)_6^{4-}$ involve transition metal–carbon coordination. Good evidence for this type of bonding was obtained from neutron diffraction experiments on $K_3Co(CN)_6$.[22] Chemical and infrared data lead to the same conclusion.[23] Also, it may be argued that the very high ligand field strength of cyanide as evidenced by magnetic and spectroscopic properties of simple cyanide complexes is consistent with C coordination, but unlikely if N coordination were the case. This last argument is placed on very firm ground by the rela-

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(20) (a) Reference 16, p. 111; (b) F. A. Cotton and M. Goodgame, *J. Am. Chem. Soc.*, **83**, 1777 (1961); (c) Professor R. S. Drago has informed us that he finds a similar *Dq* value for nitriles. This is particularly interesting, since the nitrogen in cyanide is much more basic than the nitrogen in nitriles (*e.g.*, ref. 5).

(21) (a) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, New York, N. Y., 1963, p. 166; (b) D. A. Dows, A. Haim, and W. K. Wilmarth, *J. Inorg. Nucl. Chem.*, **21**, 33 (1961).

(22) N. A. Curry and W. A. Runciman, *Acta Cryst.*, **12**, 674 (1959).

(23) (a) T. Moeller, "Inorganic Chemistry," John Wiley and Sons, New York, N. Y., 1952, p. 719; (b) L. H. Jones, *J. Chem. Phys.*, **26**, 1578 (1957).

tively low ligand field strength found by us for the nitrogen end of cyanide.

Structures of Cyanide Polymers.—The occurrence of face-centered cubic metal cyanide polymers is widespread,[3] and this raises the question as to whether there might not be some general principles that govern which of the metals will assume octahedral coordination to carbon and which will prefer nitrogen coordination. The simple six-coordinated cyanide complexes of the first transition series correlate with the electronic structure of the central metal. From d^1 through d^6 the low-energy t_{2g} levels of an octahedral complex are occupied; however, beyond d^6 added electrons occupy energetically unfavorable e_g levels which are directed toward the ligands. Thus, it is reasonable that d^7–d^9 cyanide complexes display coordination numbers less than six. Since the ligand field strength of nitrogen is much lower than that of carbon, divalent first transition series ions may be expected to form relatively stable spin-free six-coordinate species with $-NC^-$. From these considerations mixed complexes with M^{2+} (where $M^{2+} > d^6$) and M'^{2+} (where $M'^{2+} \leq d^6$) should occur with M^{2+} in the nitrogen octahedra and M'^{2+} in the carbon octahedra. It is interesting to put these arguments on a more quantitative basis, and some tentative estimates of site preference energies (SPE) were made by setting the SPE equal to the difference in crystal field stabilization energy (CFSE) of the most stable structure and that of the next most stable structure. Predictions based on these estimates were encouraging, since there was only one disagreement out of eight comparisons with observed structures.[1]

The familiar double humped curve which represents the variation of hydration energy with the number of d electrons in the first transition series is made up of a monotonic part which increases from left to right across the series and the crystal field stabilization part which gives the humps.[24] This monotonic energy contribution was neglected in our previous SPE calculation. For the purpose of predicting site preferences the monotonic part was handled empirically. Surprisingly, the data of Guzzetta and Hadley show that the monotonic part of the heat of coordination to $-CN^-$ is nearly parallel to the monotonic part of the hydration energy for divalent first transition metals.[25] The data of George and McClure also show this same (near) parallelism for a variety of ligands.[26] On the basis of this information, the reasonable assumption is made that the monotonic variation for $-NC$ coordination parallels that of $-CN^-$ coordination.[27] We assume a similar parallelism for the $+3$ ions. Comparison of heats of hydration of $+2$ and $+3$ metals[26] shows that from Cr onward the monotonic part of the heat of hydration of $+3$ metals has a slope twice that of the $+2$ metals.

From these observations and assumptions the heat of coordination for a divalent, gaseous, metal ion in the nitrogen octahedron is

$$N_M = E_N + n_M S + \delta H_{M,N} \qquad (1)$$

The first two terms describe the monotonic variation where E_N is a constant and $n_M S$ is the number of d electrons (n_M) present in M^{2+} times the slope (S) of the monotonic curve. From hydration energies S is found to be 3300 cm.$^{-1}$ per electron. The δH term is the crystal field stabilization energy of the nitrogen-coordinated metal ion. An analogous equation may be written for the heat of coordination of a carbon-coordinated divalent metal. When equations of the form of (1) are used in a thermochemical cycle for the permutation of two different divalent ions, the site preference energy of one structure over the other depends only on the difference in crystal field stabilization energies between the structures, since terms involving the monotonic variation cancel.[28]

The analog of eq. 1 for trivalent ions involves a slope of 6600 cm.$^{-1}$. Again the interchange of two different trivalent ions leads to an SPE equal to the difference in crystal field stabilization energies. When a divalent and a trivalent ion of different elements are involved four different structures may be written. The site preference energies between any two of these structures are more complex than in the previous examples. For example, a simple electron transfer leads to the most complex expression

$$\text{SPE} = (\epsilon_C - \epsilon_N + E_N - E_C) + S\delta n + \delta(\text{CFSE}) + \delta I \qquad (2)$$

The first term on the right-hand side involves differences in intercept terms for the trivalent (ϵ) and divalent (E) ions, the second term includes the difference in number of d electrons for the divalent states of the two metals (δn), and the last term is the difference in gas phase ionization potentials. The ($\epsilon_C - \epsilon_N + E_N - E_C$) term cannot be estimated from available data but it is probably small and was therefore neglected.

Table III presents the structures predicted to be the most stable along with the site preference energies favoring these structures over the next most stable ones. Comparison of these results with known structures (Table III) shows that the simple calculations

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(24) (a) O. G. Holmes and D. S. McClure, *J. Chem. Phys.*, **26**, 1686 (1957); (b) L. E. Orgel, *J. Chem. Soc.*, 4756 (1952).

(25) F. H. Guzzetta and W. B. Hadley, *Inorg. Chem.*, **3**, 259 (1964).

(26) P. George and D. S. McClure, *Progr. Inorg. Chem.*, **1**, 381 (1959).

(27) The monotonic variation is assumed to be linear in our treatment. This is not strictly correct, especially for trivalent ions, but the assumption is not too serious over the limited range of the transition series which we are considering.

(28) The crystal field stabilization energies were calculated by standard methods (ref. 26). *Dq* for the nitrogen end of cyanide was estimated for ions other than Ni^{2+} by Jørgensen's procedure (ref. 16, p. 113). For the carbon end of cyanide, data of Gray and Beach (ref. 17b) and Guzzetta and Hadley (ref. 25) were put on a common scale: Cr^{2+} 3250; Mn^{2+} 3080; Fe^{2+} 3140; Co^{2+} 3200; Ni^{2+} est. 3000; Cu^{2+} est. 3200; Cr^{3+} 2670; Mn^{3+} 3000; Fe^{3+} 3495; Co^{3+} 3350; Ni^{3+} est. 3000; Cu^{3+} est. energies given by J. S. Griffith [*J. Inorg. Nucl. Chem.*, **2**, 229 (1956)] were reduced by 50%. The magnitude of this reduction agrees with spectral data on cyanide complexes (ref. 16, pp. 110, 111). Ionization potentials used in some of the calculations were those of C. E. Moore ["Atomic Energy Levels," Vol. 2, Circular 467, National Bureau of Standards, Washington, D. C., 1952)]. The N-coordinated metal was assumed to be high spin and the C-coordinated metal low spin.

are reasonably accurate.[29] The previously stated rule, d^1 through d^6 ions should occur in carbon octahedra in preference to d^7 through d^{10} ions, is followed in observed structures and also by the calculations except for the Cr^{3+}–Ni^{2+} and Cr^{3+}–Cu^{2+} pairs.

TABLE III

COMPARISON OF OBSERVED AND PREDICTED STRUCTURES

Prediction			Observation[a]		
Metal in			Metal in		
N hole	C hole	SPE, cm.$^{-1}$	N hole	C hole	Ref.
Cr^{3+}	Fe^{2+}	23,435	Cr^{3+}	Fe^{2+}	This work
Mn^{3+}	Fe^{2+}	4,695	Mn^{2+}	Fe^{3+}	4a, 14a
Co^{2+}	Fe^{3+}	517	Fe^{2+}	Co^{3+}	4a, 14b
Ni^{2+}	Fe^{3+}	15,900	Ni^{2+}	Fe^{3+}	4a
Cu^{2+}	Fe^{3+}	7,453	Cu^{2+}	Fe^{3+}	4a
Zn^{2+}	Fe^{3+}	30,040	Zn^{2+}	Fe^{3+}	4a
Fe^{3+}	Fe^{2+}	12,944	Fe^{3+}	Fe^{2+}	4a, 4b, 4c, 4d
Cr^{3+}	Co^{2+}	12,231	M^{3+}	M^{3+}	This work
Mn^{2+}	Co^{3+}	6,513	Mn^{2+}	Co^{3+}	This work
Co^{2+}	Co^{3+}	11,725	Co^{2+}	Co^{3+}	14b, this work
Ni^{2+}	Co^{3+}	26,400	Ni^{2+}	Co^{3+}	14a, 14b
Cu^{2+}	Co^{3+}	18,661	Cu^{2+}	Co^{3+}	This work
Zn^{2+}	Co^{3+}	41,250	Zn^{2+}	Co^{3+}	This work
Cr^{3+}	Mn^{2+}	24,490	M^{3+}	M^{3+}	This work
Cr^{3+}	Ni^{2+}	16,560	Ni^{2+}	Cr^{3+}	This work
Cr^{3+}	Cu^{2+}	2,664	Mixed?		This work
Zn^{2+}	Cr^{3+}	7,440	Zn^{2+}	Cr^{3+}	This work

[a] Structural inferences from infrared spectra (ref. 4a and this work) serve only to show the oxidation state of the carbon-coordinated metal. In a number of cases this information, along with colors and visible absorption spectra, serves to define the structure, *e.g.*, nickel cobalticyanide.

Cyanide Linkage Isomerism.—On the basis of the above calculations, it appeared that $KFe^{II}Cr^{III}(CN)_6$ would be less stable than $KCr^{III}Fe^{II}(CN)_6$. Since $Cr(CN)_6^{-3}$ is kinetically rather inert,[30] this system seemed to offer the possibility of observing both the stable and metastable forms. When a solution of $K_3Cr(CN)_6$ is mixed with a ferrous solution, a brick-red precipitate forms, which displays infrared bands at 2168 (s) and 2114 (w) cm.$^{-1}$. The position of the strong band is similar to that of other transition metal chromicyanides (*e.g.*, manganese chromicyanide, 2166; and zinc chromicyanide, 2178 cm.$^{-1}$). The visible and ultraviolet spectrum contains bands at 195 (s), 256 (sh), and 447 (m) mμ. When this material is heated at 100° the color changes to dark green. An infrared spectrum revealed a shift in C≡N stretching frequency to 2092 cm.$^{-1}$, and this latter frequency is characteristic of ferrocyanides. The electronic spectrum shows bands at 226 (m), 300 (sh), and 428 (s) mμ. The first two of these probably correspond to d–d transitions for Fe(II) in ferrocyanide and they are observed in similar positions for $K_2CuFe(CN)_6$ (*ca.* 220 and *ca.* 310 mμ) and for $K_2NiFe(CN)_6$ (*ca.* 222 and 310 mμ). It appears that, in effect, a C≡N flip has occurred.[31]

$$KFeCr(CN)_6 \xrightarrow{\Delta} KCrFe(CN)_6$$

To our knowledge, this is the first evidence for linkage isomerism in a cyanide complex.[32]

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(29) Dr. A. Vlček has pointed out that in some of the cyanide polymers it may not be meaningful to assign formal oxidation states to the metals because the –metal—C≡N—metal– system may only be accurately described by molecular orbitals which pervade the crystal (an energy band). This would arise from overlap of metal t_{2g} orbitals with cyanide π^*-orbitals. An additional requirement is a good energy match between the C-coordinated metal orbitals and those of the N-coordinated metal. Robin has considered this problem for Prussian blue (ref. 4b), where he estimates that the optical electrons are 99% localized. In many cases, such as zinc ferrocyanide and nickel ferrocyanide, the energy mismatch is undoubtedly so great that the localized picture is accurate, but for some of the systems this may not be the case.

(30) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, New York, N. Y., 1958, p. 398.

(31) The possibility that the isomerism reaction involved an oxidation and reduction seems unlikely from oxidation potentials for the aqueous ions

$$Cr(CN)_6^{-3} + Fe^{2+} = Fe^{3+} + Cr(CN)_6^{4-} \quad E^\circ \ -1.8 \text{ v.}$$

Also, the rate of electron transfer in the solid should be very rapid; this would preclude the isolation of two "oxidation–reduction isomers."

(32) Professor J. C. Bailar, Jr., has informed us that he has obtained evidence for a cyanide flip in heavy metal cyanide polymers.